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(21) International Application Number: PCT/US97/05432 (22) International Filing Date: 1 April 1997 (01.04.97) (30) Priority Data: 08/627,769 1 April 1996 (01.04.96) US (71) Applicant: CASE WESTERN RESERVE UNIVERSITY [US/US]; 10900 Euclid Avenue, Cleveland, OH 44106 (US). (72) Inventors: SAVINELL, Robert, F.; 34504 Bramble Lane, Solon, OH 44139 (US). LITT, Morton, H.; 2575 Charney Road, University Heights, OH 44118 (US). (74) Agent: MINNICH, Richard, J.; Fay, Sharpe, Beall, Fagan, Minnich & McKee, Suite 700, 1100 Superior Avenue, Cleveland, OH 44114-2518 (US).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROTON CONDUCTING POLYMER ELECTROLYTES PREPARED BY DIRECT ACID CASTING (57) Abstract A method for casting solid polymer electrolyte membranes comprising proton conducting polymers stable at temperatures in excess of 100 °C directly from acid solution. The invention further relates to the enhanced performance of these membranes with respect to conductivity. Particularly, the invention relates to the use of trifluoroacetic acid (TFA) as an acid solvent doped with H ₃ PO ₄ from which polybenzimidazole (PBI) solid polymer electrolyte membranes may be cast.		

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PROTON CONDUCTING POLYMER ELECTROLYTES PREPARED BY DIRECT ACID CASTING

Field of the Invention

The invention relates to a method for casting a solid polymer electrolyte useful in fuel cells operated at elevated temperatures. More specifically, the invention is related to the use of a method of casting polymer electrolyte membranes intended for use in fuel cells operating on liquid fuels, the casting method involving casting the polymer electrolyte membrane directly from an acid solution. The membranes cast by this method demonstrate unexpectedly improved conductivity.

Background of the Invention

In the past decade considerable effort has gone into the development and characterization of perfluorosulfonic acid polymer electrolytes such as Nafion. These efforts have shown that polymer electrolyte membranes (PEM) offer a number of advantages over conventional electrolytes when used in electrochemical devices such as fuel cells and water electrolyzers.

U.S. Serial No. 08/332,869, entitled "Proton Conducting Polymers", the disclosure of which is incorporated herein by reference, discloses the use of

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polymer electrolyte membranes, for example polybenzimidazole (PBI) doped with phosphoric acid, which are capable of conducting protons at temperatures of up to at least 200°C. These membranes, therefor, 5 avoid prior art problems related to dehydration of the membrane. Further, disadvantages due to poisoning of the electrode catalysts and fuel crossover are overcome by the novel polymer electrolyte membranes disclosed in the patent. The preparation of the membranes of the 10 patent involves first casting the membrane film from an appropriate solution, such as dimethyl acetamide (DMAc), and then doping the film with the desired acid constituent. Conductivity in the range of from 0.01 to 0.04 S/cm for temperatures from 130°C - 190°C and water 15 vapor partial pressures up to 1 atmosphere were recorded for H₃PO₄ doped PBI films.

It has now been discovered that the conductivity of polymer electrolyte membranes of the type discussed above may be significantly and unexpectedly enhanced by 20 preparation of the membrane from a solution of the doped polymer in an acid. For example, a PBI film doped with H₃PO₄ and prepared from trifluoroacetic acid (TFA) solution exhibits conductivity measured at 0.04-0.08 S/cm, as compared to the lower conductivity measured for 25 PBI membranes cast from DMAc and subsequently doped.

It has further been discovered that the economics of membrane production can be reduced by casting the PBI membranes directly from a casting solution containing

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H₃PO₄ and including trifluoroacetic acid (TFA) as a solvent.

It is, therefore, an object of the subject invention to provide a method for casting a solid
5 polymer electrolyte membrane which does not suffer from known problems associated with catalyst stability and activity, and which demonstrates enhanced conductivity.

It is another object of the invention to provide a casting solution from which a solid polymer electrolyte
10 membrane which is suitable for use in direct methanol fuel cells without exhibiting high methanol permeability resulting in loss in efficiency due to methanol crossover can be produced by direct casting methods.

Summary of the Invention

15 The subject invention relates to a method for casting solid polymer electrolyte membranes comprising proton conducting polymers stable at temperatures in excess of 100°C directly from acid solution. The invention further relates to the enhanced performance of
20 these membranes with respect to conductivity. Particularly, the invention relates to the use of trifluoroacetic acid (TFA) as an acid solvent doped with H₃PO₄ from which polybenzimidazole (PBI) solid polymer electrolyte membranes may be cast.

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Brief Description of the Drawings

FIGURE 1 is a graph showing the conductivity as a function of water vapor activity for DMAc cast PEMs;

FIGURE 2 is a graph showing the conductivity as a function of water vapor activity for PEMs comparable to that of FIGURE 1, but cast from acid solution according to the invention; and,

FIGURE 3 is a graph showing the conductivity as a function of temperature of films cast from acid solution and from DMAc.

Detailed Description of the Invention

The invention relates to novel solid polymer electrolytes cast directly from acid solution and to the significantly enhanced conductivity of such solid polymer electrolytes. These membranes exhibit stability at temperatures up to at least 200°C to overcome known catalyst stability and conductivity problems. Specifically, the invention relates to polybenzimidazole film doped with H_3PO_4 cast directly from trifluoroacetic acid solution in combination with phosphoric acid. The resulting membrane is suitable for use as a solid polymer electrolyte membrane in methanol-air fuel cells. These polymer films exhibit excellent oxidative and thermal stability, these properties being further enhanced by the acid nature of the polymer.

The subject solid polymer electrolyte membrane exhibits stable chemical and electrical properties at

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temperatures well above 100°C and up to at least 200°C, has good mechanical and film properties, demonstrates high proton conductivity and low fuel permeability, and is capable of conducting protons with very low water activity.

The polymer used in the subject invention is preferably polybenzimidazole (PBI), but may be any polymer known to the skilled artisan which is soluble in the TFA/H₃PO₄ acid casting solution. Other polymers which may be suitable may be found in the disclosure of U.S. Serial No. 08/332,869.

PBI's are known to have excellent oxidative and thermal stability, and are further stabilized by reaction with the doping acid in the acid casting solution. Proton hopping between basic sites on the polymer compound and/or the imbibed free acid provides enhanced ionic conductivity. Further, the barrier properties of these films are enhanced due to the single phase morphology of the material, as compared to the biphasic nature of the non-polar fluorocarbon/polar ionic membranes. "Single phase morphology" refers to a microscopic continuous matrix of a single material as contrasted to a two-phase system of a polar phase mixed with a non-polar phase.

In operation in a fuel cell utilizing a suitable fuel, such as methanol, the PBI polymer electrolyte membrane conducts protons from the fuel electrode to the oxygen cathode. Carbon monoxide, present in fuels like

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reformed hydrogen, poisons the platinum catalyst commonly used in fuel cells. Liquid fuels like methanol produce even more severe poisoning effects because carbon monoxide is an intermediate in the fuel oxidation
5 process. However, at higher temperatures, approaching 200°C, the cell operation stimulates carbon monoxide oxidation to carbon dioxide, resulting in substantially enhanced catalyst activity in spite of the poisoning effect of the carbon monoxide.

10 The invention will now be discussed with reference to the preferred embodiment of the invention, i.e. casting of the PBI film from TFA/H₃PO₄ solution. The following examples and related test data are intended to be merely exemplary and in no way intended to be
15 limitative of the subject invention. Viable variations of the parameters presented, as well as other aspects of the materials, their preparation and their use, will be apparent to those skilled in the art and are intended to be covered by this specification and the appended claims
20 if falling within the meets and bounds thereof.

PEM Preparation

Films of polybenzimidazole were prepared by dissolving the polymer PBI (20 wt.%) in trifluoroacetic acid. This solution contained two phases. Phosphoric
25 acid was then added to the solution, and the solution become homogenous. The solution was then filtered and cast on a clean glass plate using a Gardner knife. The

film was heated at 140°C in air for fifteen (15) minutes. It was removed from the glass plate and heated in a vacuum oven overnight at 90°C to dry the film.

Conductivity Measurements

5 Conductivity measurements were made with a four point probe apparatus. In this apparatus, two platinum foil electrodes were clamped to the end of a 3cm(L) x 0.5cm(W) polymer sample. These electrodes were used to pass current through the sample. The magnitude and
10 frequency of the applied current were controlled using a PAR 173 potentiostat/galvanostat and a Wavetek 185 signal generator. Two platinum wires (0.5mm diameter), spaced 1cm apart, were used to measure the voltage drop at the center of the sample. Voltage measurements were
15 made at three or more current levels to ensure that the voltage-current behavior was ohmic. The current was applied at two different frequencies, 100 and 1000Hz. No frequency dependence was observed. The entire apparatus was contained within a stainless steel vessel,
20 which was placed inside an oven and connected to a gas manifold system so that the temperature, pressure and composition of the gas phase in contact with the sample could be controlled. Measurements as a function of water partial pressure above 100°C were performed by
25 partially evacuating the cell and then injecting sufficient liquid water via a septum to yield the desired water partial pressure.

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Samples were prepared from a solution of the polymer and phosphoric acid in trifluoroacetic acid (TFA). Initial measurements of the conductivity of the samples cast from trifluoroacetic acid indicated
5 considerably higher values than those of the samples cast, for instance, from dimethylacetamides (DMAc), as in U.S. Serial No. 08/332,869, referred to hereinabove. The results from the conductivity measurements of these samples are presented in Table I, along with
10 representative values for the previous samples cast from DMAc. It is clear from the results in this table that the films cast from TFA are significantly more conductive than the films cast from DMAc. In addition, films of both 1 mil and 4 mil thicknesses yielded
15 similar conductivities. For both types of samples, the conductivity increases with increasing acid content, with increasing water vapor activity and with increasing temperature. There are indications that the conductivity drops when the sample is held at a high
20 temperature overnight (compare the starred values to non-starred values at similar temperatures and water vapor activities). However, even after these drops, the conductivity of the TFA samples is considerably higher than that of the DMAc samples.

Tabl I

Conductivity of Polybenzimidazole Samples Cast from
TFA/H₃PO₄ and H₃PO₄ doped PBI Cast from DMAc

	Casting Solvent	H ₃ PO ₄ Content mol/l	Temperature °C	Water Vapor Activity	Conductivity S/cm
5	TFA	480	130	0.055	0.031
	TFA	480	130	0.098	0.039
	TFA	580	130	0.13	0.055
	TFA, 4 mil	580	130	0.149	0.075
10	TFA	580	130	0.173	0.052
	TFA	580	130	0.19	0.072
	DMAc	501	130	0.1	0.01
	DMAc	501	130	0.25	0.02
	TFA	580	150	0.03	0.043*
15	TFA	580	150	0.05	0.052*
	TFA	580	150	0.08	0.056
	TFA	580	150	0.11	0.048
	TFA	580	150	0.16	0.083
	DMAc	501	150	0.12	0.022
20	DMAc	501	150	0.20	0.03
	TFA, 4 mil	580	170	0.04	0.074
	TFA	580	170	0.05	0.053
	TFA	580	190	0.02	0.060*
	TFA, 4 mil	580	195	0.017	0.068
25	TFA, 4 mil	580	195	0.024	0.078
	TFA, 4 mil	580	195	0.025	0.049*
	TFA, 4 mil	580	195	0.044	0.083
	TFA, 4 mil	580	195	0.072	0.068*
	DMAc	501	190	0.04	0.023
30	DMAc	501	190	0.12	0.040

Samples are 1 mil thick unless otherwise noted

* - Value obtained after sample had been at temperature for over 16 hours.

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Since the addition of a stronger acid (i.e. trifluoroacetic acid) appeared to improve the conductivity of the PBI/H₃PO₄ system, additional samples were prepared containing two other strong acids, hexafluoroglutaric acid (HFGA) and squaric acid (SA). Conductivity results for these samples are given in Table II and Table III. In comparing these results to those given in Table I, it appears that not all acids yield higher conductivities. It is further noted, however, that in some instances (Table III particularly) where the mol% of H₃PO₄ was lowered due to the addition of another acid, while the conductivities are lower than those reported in Table I for TFA, they are nonetheless as good as, or better than those reported in Table I for DMAc membranes.

Table II

Conductivity of Polybenzimidazole Samples Cast from TFA/H₃PO₄ and HFGA

H ₃ PO ₄ Content mol%	Temperature °C	Water Vapor Activity	Conductivity S/cm
<365	130	0.165	0.008
<365	150	0.056	0.006
<365	170	0.026	0.005
365	130	0.151	0.017
365	150	0.071	0.017
450	130	0.110	0.031

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Table III

Conductivity of Polybenzimidazole Samples Cast from
TFA/H₃PO₄ and Squaric Acid

H ₃ PO ₄ Content mol%	Temperature °C	Water Vapor Activity	Conductivity S/cm
450	150	0.05	0.025
450	150	0.067	0.028
450	150	0.089	0.028*
450	150	0.094	0.030
450	150	0.143	0.034
450	190	0.017	0.021*
450	190	0.035	0.035*
450	190	0.058	0.033*

* - Value obtained after sample had been at temperature for over 16 hours.

FIGURE 1 is a graph illustrating conductivity results for PBI films containing 501 mol% H₃PO₄ cast from DMAc. FIGURE 2 is a similar graph which demonstrates conductivity as a function of water vapor activity for the preferred PBI film containing 580 mol % H₃PO₄ cast from a TFA/H₃PO₄ solution. FIGURE 3 is a graph comparing the conductivity of these same films as a function of temperature where the upper curve represents a film cast from acid solution according to the invention and the lower curve represents the conductivity of a film cast from DMAc. A marked increase in conductivity, between two (2) and five (5) fold, is shown.

Casting Films of Varying Thickness

The ability to cast PBI films from TFA with varying H₃PO₄ concentration was also evaluated. In conducting this evaluation, PBI/TFA solutions were prepared using

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different molecular weight PBI's and including different H_3PO_4 ratios. Film 1 was cast in a special acid resistant hood, but with no protection to ensure slow TFA evaporation. Films 2-10 were cast from the solutions in a glove box in the hood. Table IV reports the results of these casting exercises. These results demonstrate the mechanical properties of the film, in terms of flexibility and inherent viscosity, η_{inh} , which is defined as follows:

$$\eta_{inh} = \ln(\eta_{rel})/c$$

wherein $\eta_{rel} = \eta/\eta_0$, where η is flow time of the polymer solution, η_0 is flow time of pure solvent and c is 0.5 gm/100ml solvent.

TABLE IV

PBI/ H_2PO_4 Films Cast from TFA Solutions

Film No.	η_{inh} of PBI dl/gram ^a	Content of H_3PO_4 (M%)	Thickness (mil)	Properties
1	1.26	600	2.0	brittle
2	1.26	600	3.1	flexible
3	1.257	580	2.5	flexible
3-1	1.257	580	2.6	flexible
3-2	1.257	600	2.3	flexible
3-3	1.257	600	2.3	flexible
3-4	1.257	600	3.0	flexible
3-5	1.257	600	2.9	flexible
9	1.257	900	3.1	flexible
7-1	1.28	700	2.0	flexible
7-2	1.28	700	2.9	flexible
7-3	1.28	700	3.1	flexible
6-1	0.85	600	2.1	flexible
6-2	0.86	600	1.85	flexible
10-1	1.09	600	2.9	flexible
10-2	1.09	1000	3.0	flexible

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- ^a - The molecular weight of PBI for these inherent viscosities ranges from about 20,000 to 30,000.

As seen from the foregoing results, PBI films with
5 good mechanical properties can be cast from PBI's of
varying molecular weight, with varying ratios of H_3PO_4
and at varying thicknesses.

The invention has been described by way of example.
Obviously, modifications and alterations will occur to
10 others upon reading and understanding the preceding
detailed description. It is intended that the invention
be construed as including all such modifications and
alterations insofar as they come within the scope of the
appended claims or the equivalents therefor.

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We claim:

1. A method for casting a solid polymer electrolyte membrane, comprising:
preparing a solution of the polymer dissolved in an
5 acid solvent which further contains a doping acid;
casting the solution to produce a membrane; and
drying the cast membrane.
2. An acid solution suitable for casting as a polymer electrolyte membrane capable of achieving
10 conductivity levels 3-5 times that of similar membranes cast from non-acid solutions under similar conditions, said acid solution comprising an acid solvent capable of dissolving a polymer suitable for use as a solid polymer electrolyte, the polymer, and doping acid suitable of
15 enhancing the high temperature stability of the polymer.
3. A method for casting a solid polymer electrolyte membrane exhibiting enhanced conductivity in methanol/air fuel cell use comprising casting the polymer from a solution of TFA/H₃PO₄ at a polymer mol%
20 level of at least 300 mol%.
4. A solid polymer electrolyte membrane comprising an acid solution-cast polymer membrane capable of achieving conductivity in excess of 0.04S/cm in a methanol fuel cell at temperatures from 130-190°C

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and at water plus methanol pressures of about 1 atmosphere.

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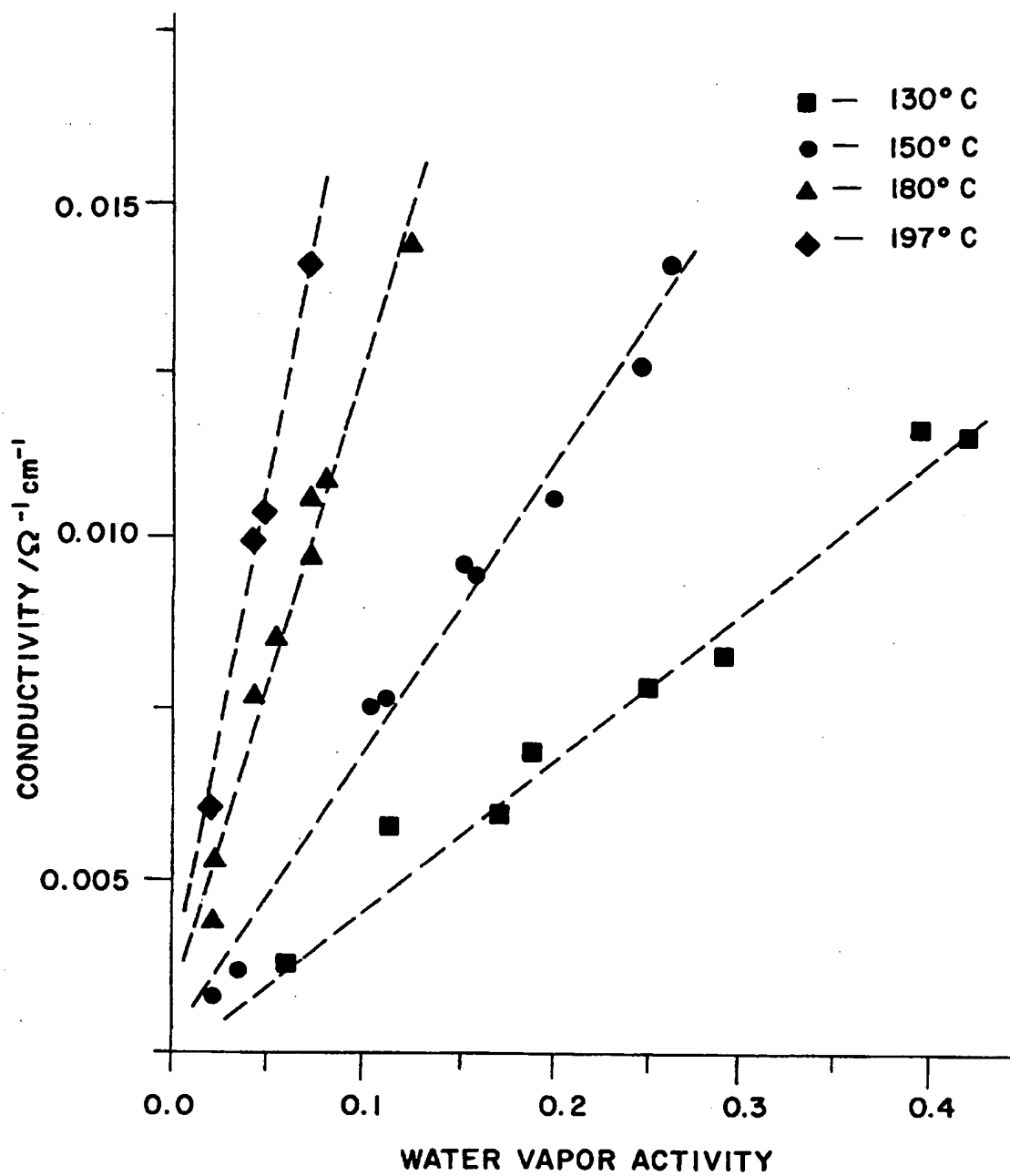


FIG. 1

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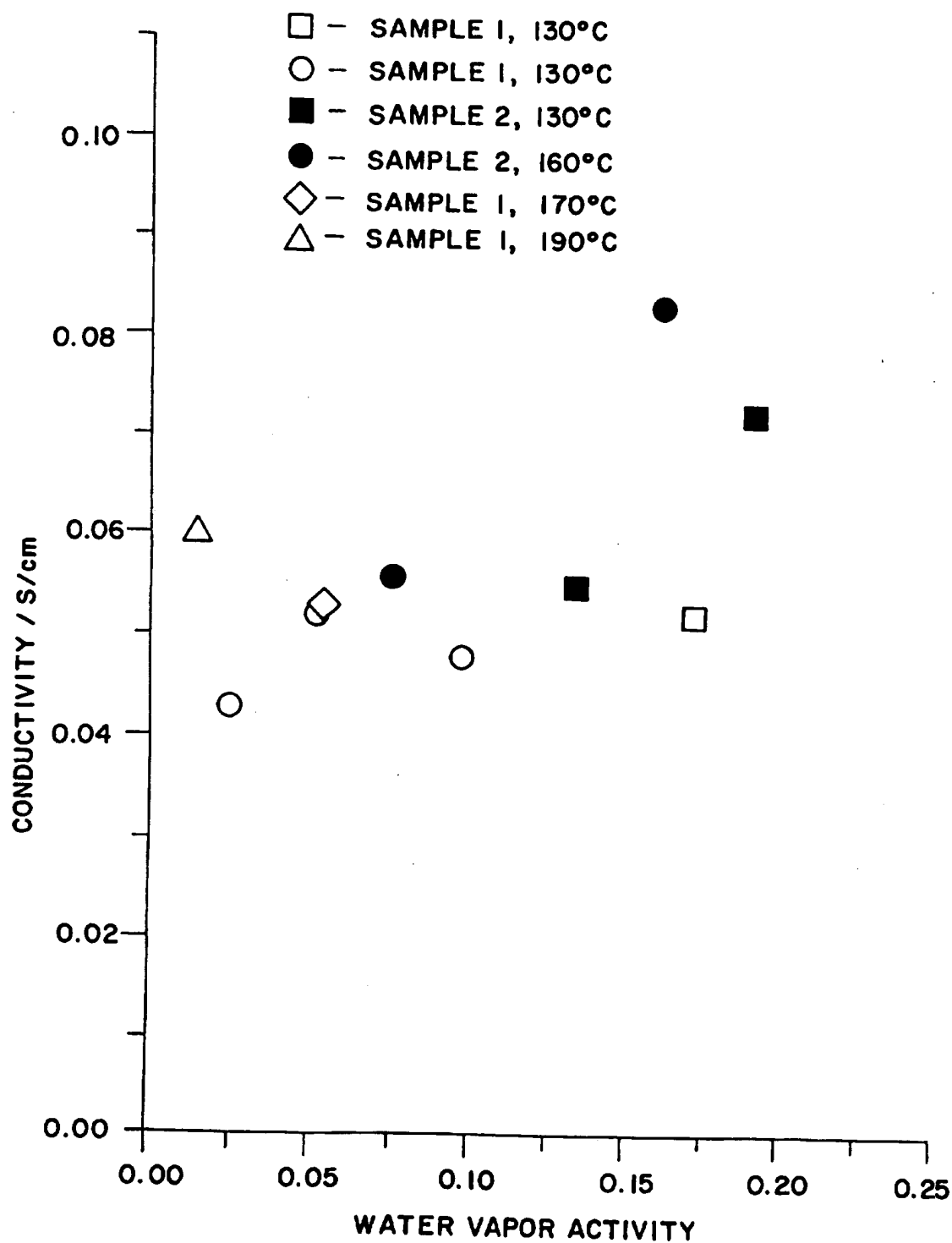


FIG. 2

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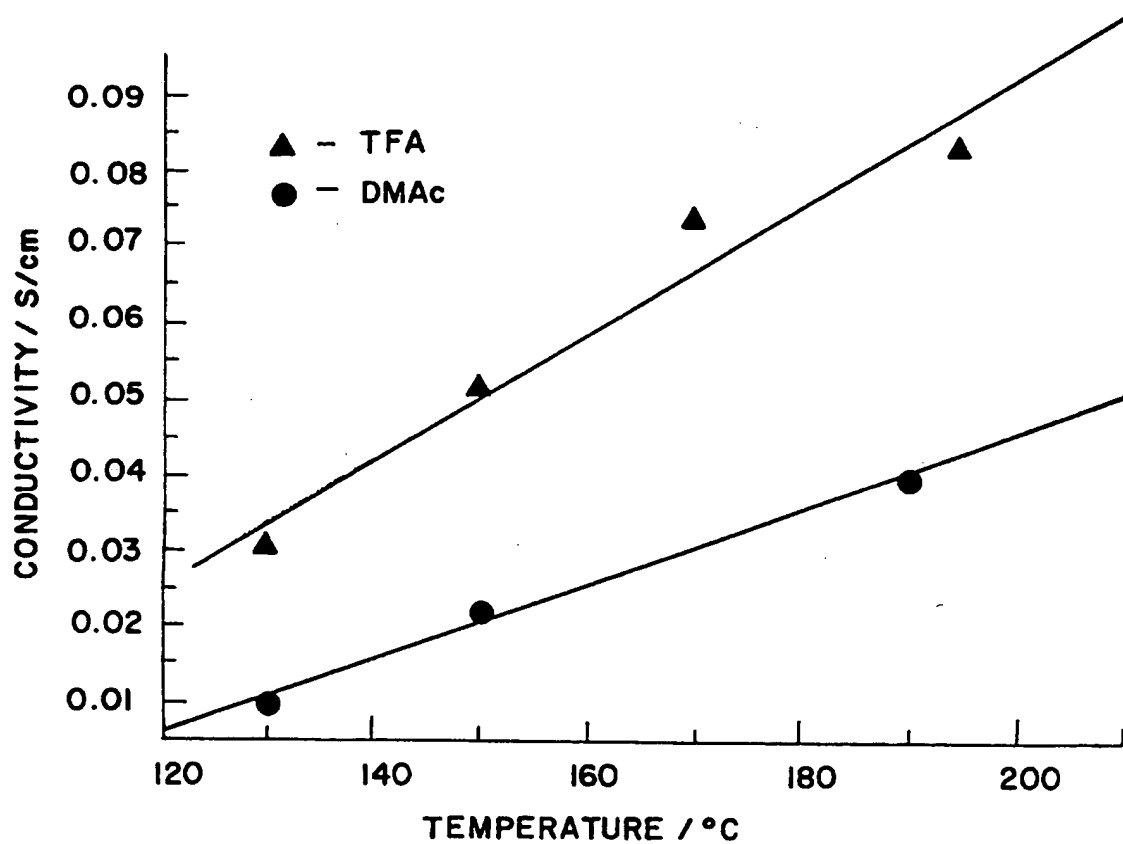


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05432

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01M 8/02, 8/10

US CL : 429/33, 189

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/33, 189, 192; 29/623.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,378,550 A (DODDAPANENI ET AL) 03 January 1995	1-4
A	US 5,429,759 A (ANDRIEU ET AL) 04 July 1995	1-4
A,P	US 5,525,436 A (SAVINELL ET AL) 11 June 1996	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 JUNE 1997

Date of mailing of the international search report

04 AUG 1997

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05432

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/05432

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1, 3 and 4, drawn to a method of making an electrolyte membrane and to the electrolyte membrane product.

Group II, claim 2, drawn to an intermediate.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the intermediate of Group II could be used in a materially environment than that of the membrane of Group I such as for use in liquid polymer investigative studies.